Corrosion of refractories and ceramic materials

Agersted, Karsten

Publication date:
2012

Corrosion

of refractories and ceramic materials

Karsten Agersted
kagn@dtu.dk
DTU Energy Conversion
Department of Energy Conversion and Storage

Outline

- Introduction, materials, fundamentals and share of experience
- Ever fascinating corrosion in glass furnaces
- Corrosion in gassification furnaces
- Aqueous corrosion of technical ceramics
- Degradation of zirconia electrolytes in solid oxide cells


Thermal Ceramics
SUPERWOOL


23

Acidity

Lewis acid-base; electron pair acceptor-donor

	Acid					Neutral
Gas	NO_x	SO_3	SO_2	CO_2	BO_x	VO_x
Solid	SiO_2	TiO_2	ZrO_2	Fe_2O_3	Cr_2O_3	Al_2O_3

	Neutral						Base	
Gas	VO_x						Na	K
Solid	Al_2O_3	FeO	NiO	MnO	MgO	CaO	Na_2O	K_2O

Refractory groups

- **Ceramic bonded**
  Some have glassy grain boundaries, some have not
  Some are very porous, some are not
  Some are “basic”, some are “acidic”, some are “neutral”

- **Chemically bonded**
  Often $MgCl_2$ and $MgSO_4$ bonded magnesite or phosphate bonded high-alumina

- **Carbon bonded**
  Often Magnesite, Magnesia, Alumina or Zircon based

- **Fused**
  Often Mullite, Alumina, Chrome-magnesite and Zirconia based

- **Monolittic; stamping, gunning, grouting**
  Often a combination of cement-bonding or phosphate bonding with pre-firing

- **Fibrous**
  Often resin- or phosphate-bonded high-temperature fibres, eg. alumina.

Binder types in refractories

- **Cements – High alumina cements; AH, AH_3, C_3AH_6, C_2AH_8, CAH_{10}**
  Magnesia cements; $MgCl_2$ and $MgSO_4$

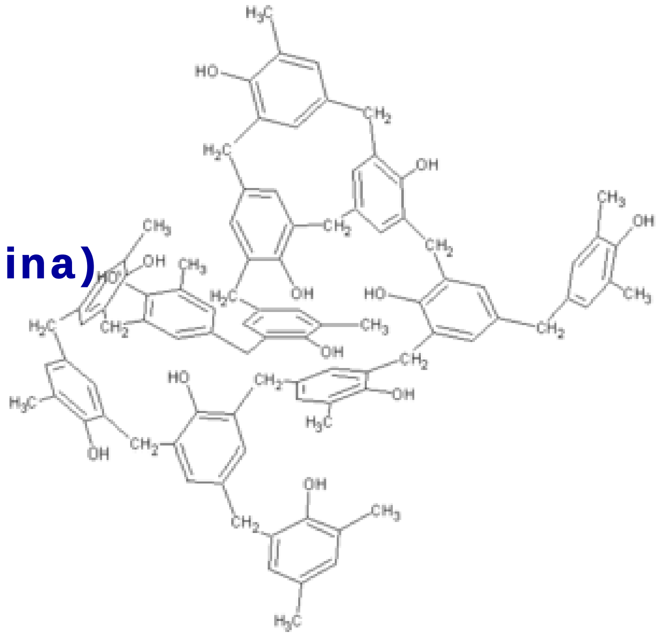
- **Phosphates – polyphosphates, $H_{n+2}P_nO_{3n+1}$,**
  Aluminium phosphate, MAP, $Al(H_2PO_4)_3$
  Sodium phosphate, "$NaCaPO_4$" w. $Mg(H_2PO_4)_2$ > MgP_2O_7
  Aluminium chloro phosphate, APCH, $Al(HPO_4)Cl{:}4H_2O$

- **Polymeric silicates; Na_2SiO_3, Si(OEt)**

- **Carbon and tar**

- **Resins; Phenol- and fural-based resins**

- **Other; Clay, Boric acid, Boehmite (Rho-alumina)**



Refractory materials

Magnesite (>60% MgO)	*Steel furnaces*
Magnesia-carbon	*High wear resistance in steel industry*
Chrome-magnesite	*Wall lining in Siemens-Martin steel furnaces*
Magnesia-alumina	*Cement furnace linings, crucible linings for steel*
Dolomite (CaMg)(CO_3)	*Slag resistant lining*
Forsterite (2MgO-SiO_2)	*Furnace lining*
Chamotte	*Cheap lining, medium temperature resistance, alkali*
Graphite-chamotte	*Crucibles for metal processing (>2000y)*
High-alumina (>45%Al)	*Versatile, higher slag resistance*
Alumina-carbon	*Used in contact with liquid metals*
Silicate	*Furnace linings, high mechanical strength at HT*
Zirconia	*Glass furnaces, tubings for metal industry, saggers*
Silicon Carbide	*Kiln furniture, aluminium industry, incinerators*
Silicon nitride	*Linings in aluminium production*

Never look only at the overall chemical composition

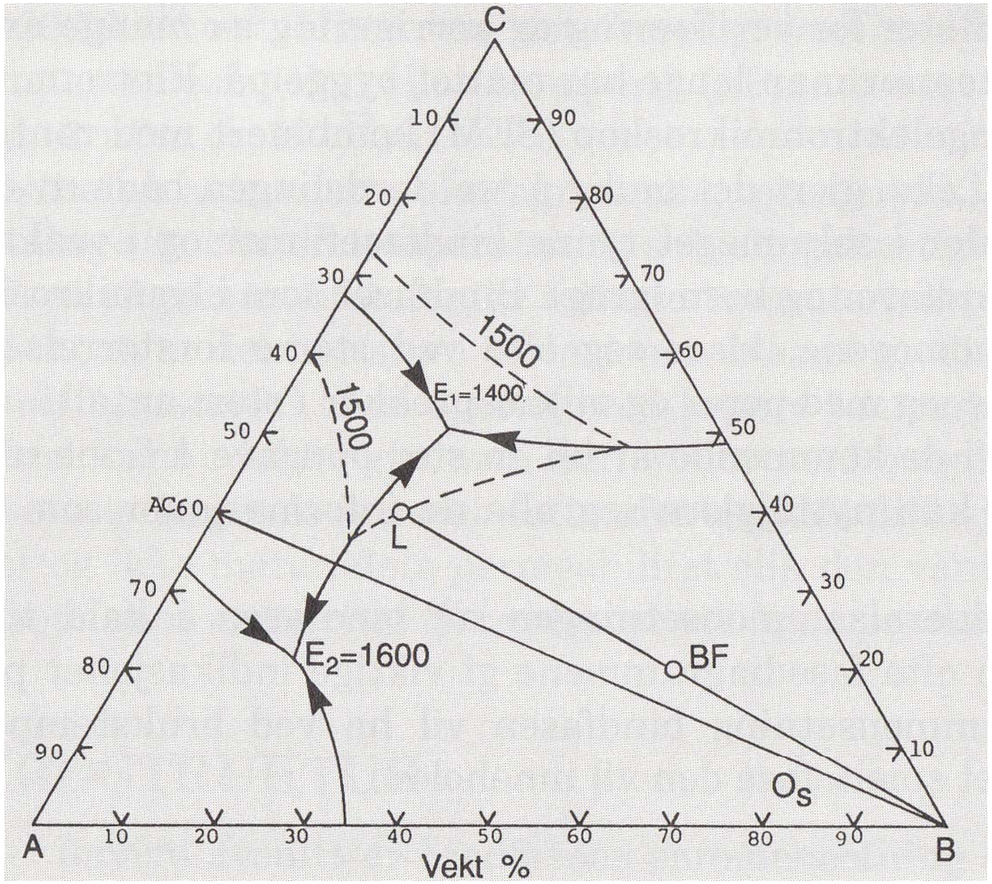
Always focus on binder phases

Material composition:
15% A, 80% B, 5% C

Binder phase composition:
20% A, 60% B, 20% C

Given that all C is in the binder phase, melt composition is: 40% A, 20% B, 40% C at operating temperature of 1500°C

All C is dissolved => liq. Phase ~50% of binder and 12.5% of the entire material



Will this material then be mechanically stable at 1500°C?

Selected "classics"

- Clay bonded SiC looses strength in reducing atmospheres
- SiC is oxidised in oxidising atmospheres
- Bursting seen in Chrome-magnesite materials on changing pO_2 ($Fe^{3+} \Leftrightarrow Fe^{2+}$)
- Reduction of free SiO_2 in chamotte materials, when the atmosphere contains hydrogen
- Volume expansion on Si-Al reactions with K from the furnace atmosphere
- Sulphur decreases oxide-melt surface tension, hence facilitate penetration

Refractories in a glass furnace

Mayne Island Glass Foundry

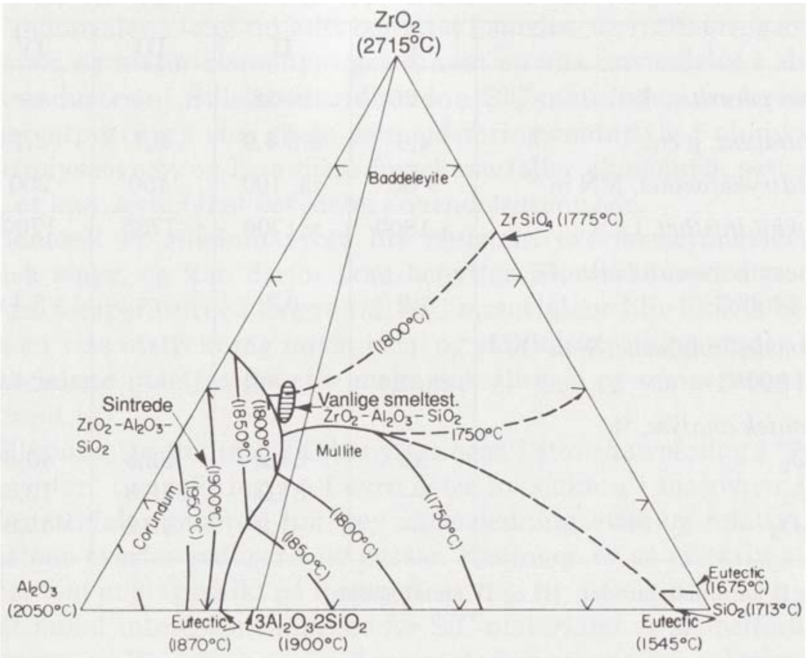
http://www.mayneislandglass.com/170lbinvestedsicfurnace.htm








Refractories in a glass furnace



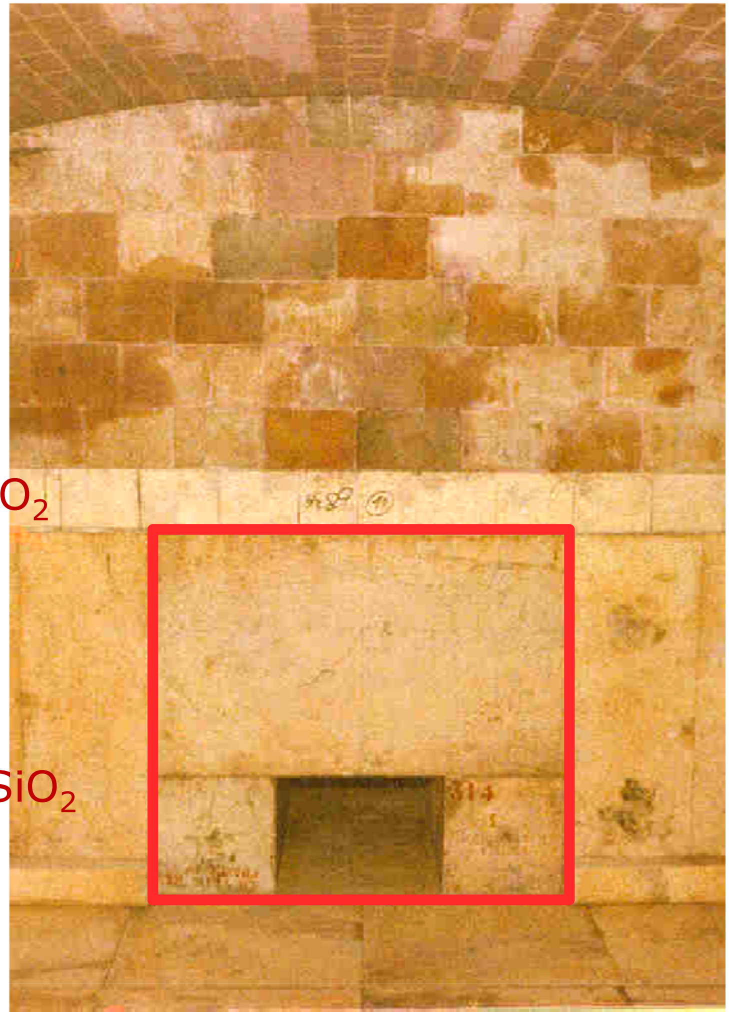
$MgO:Al_2O_3$

Fused ZrO_2

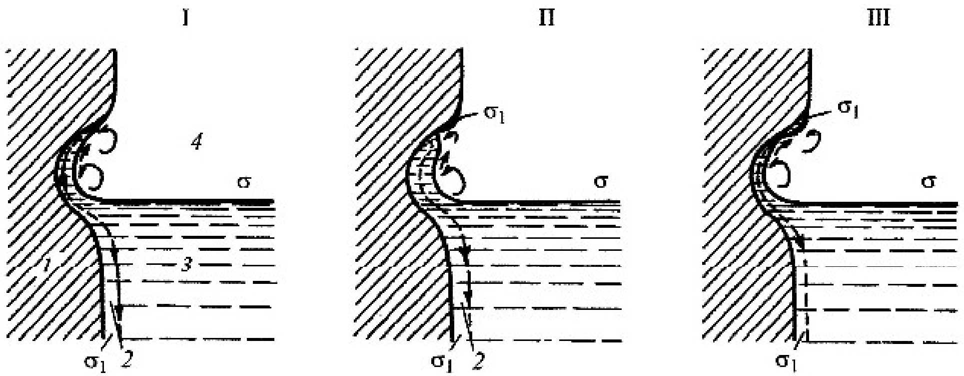
$(Cr,Al)_2O_3:ZrO_2$

$Al_2O_3:ZrO_2:SiO_2$
(BACOR)

Al_2O_3 (MgO)

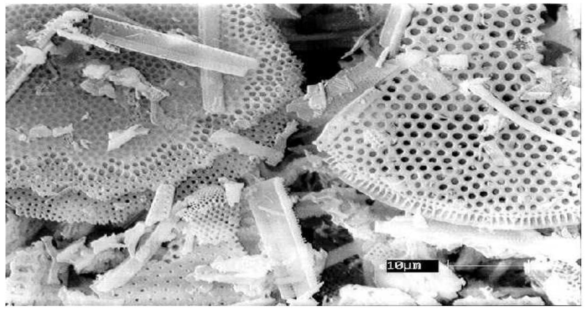


Corrosion in a production furnace for container glass



Insulating boards (Ca-Silicate and Vermiculite)
Moler insulating bricks

Are relatively cheap and robust insulating materials - of acidic behaviour.



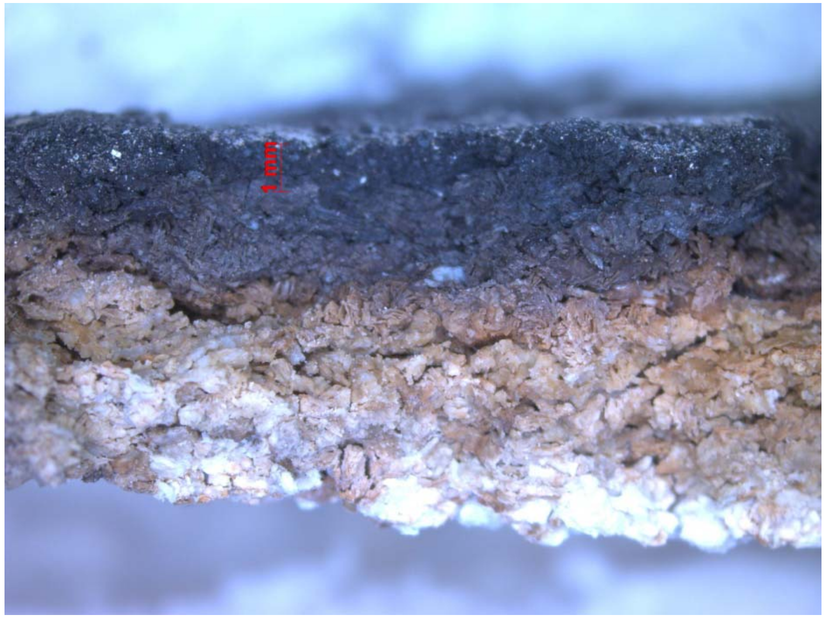
Diatomite or **kieselgur**
80 to 90% silica,
traces of clay minerals
~3% alumina and ~1% iron oxide.

Vermiculite is a group of hydrated laminar minerals which are aluminium-iron-magnesium silicates, resembling mica in appearance.
They expand 20-30 times their volume, when heated.

Two “classical” issues
Quite often seen in wood stoves

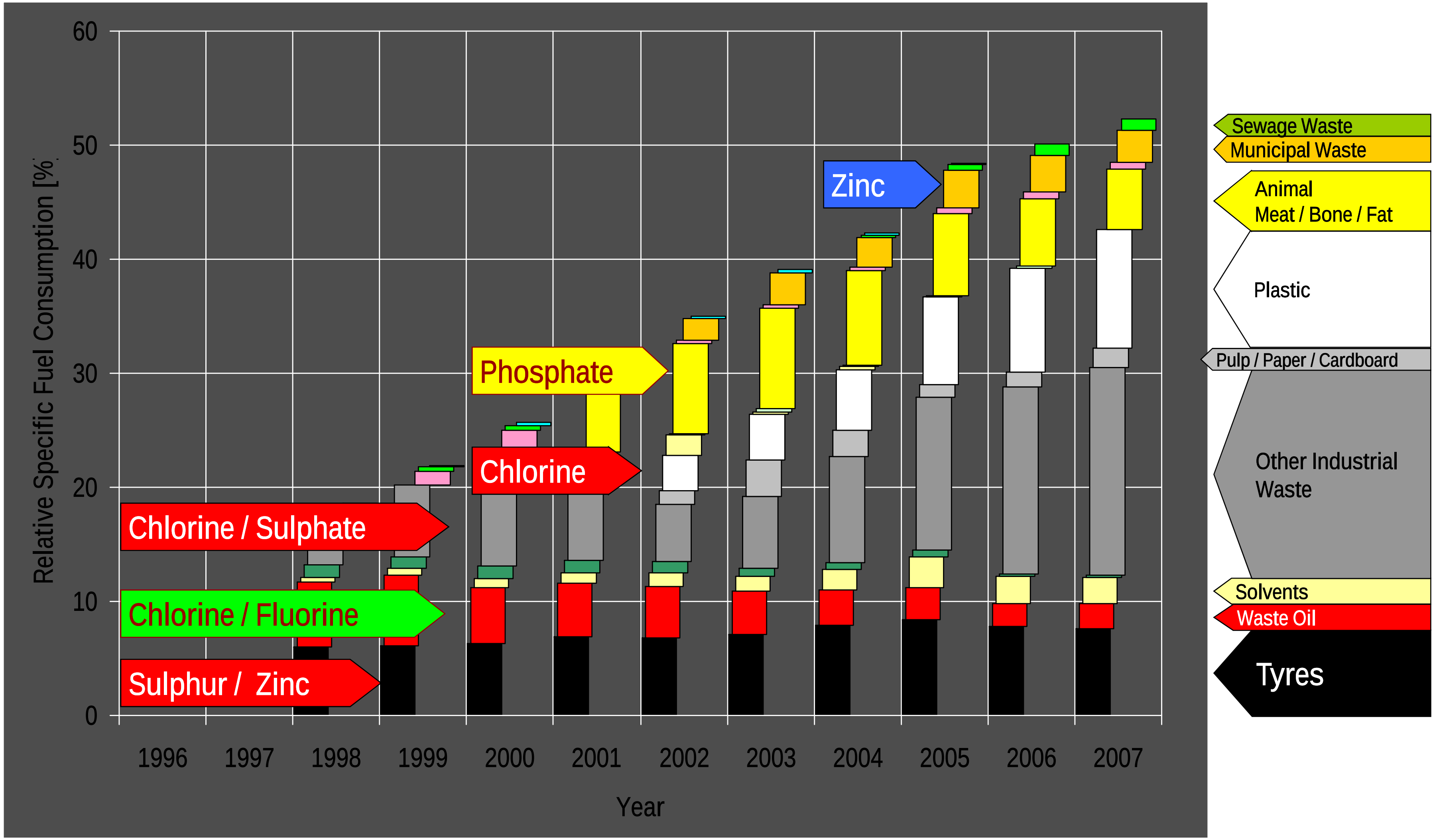
Overheating, eg. by burning coal or polymers, destroys the oven lining. Vermiculite, t > 1100°C.

Carbon deposition inside the pores of the refractory grows and causes spallation. Iron Oxide even catalyses the carbon formation from CO, which is formed when oxygen to fuel ratio is low.



On longer exposure to reduced air to fuel ratio, carbon has filled the pores of the flexible Vermiculite, hence increased the overall heat transfer. The picture shows also that the oxygen potential has been low enough to partly reduce the vermiculite material on the cold side – the pale colour.

New Challenges for Refractories with Alternate Fuels



Distribution of thermal energy consumption from alternate fuels in Germany

Adam A. Wajdowicz, Magnesita Refratarios

Corrosion issues in a gasifier furnace lining

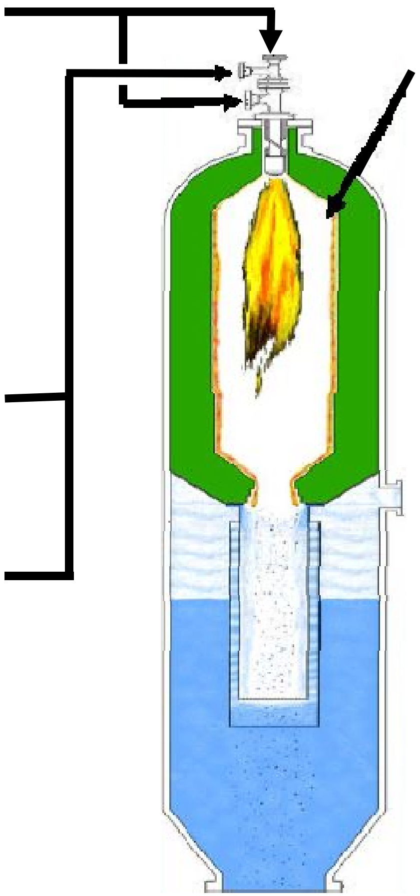
$$C + H_2O\ (gas) + O_2 \rightarrow CO + H_2 + CO_2 + \text{by-products}\ (g, s, l)$$

(H_2S, CH_4, NH_3, HCN, K, Na, Ca, Si, . . .)

Oxygen

C-source

Water



800-1275°C, 1-60 bar, slag & H_2S

Products (syngas)

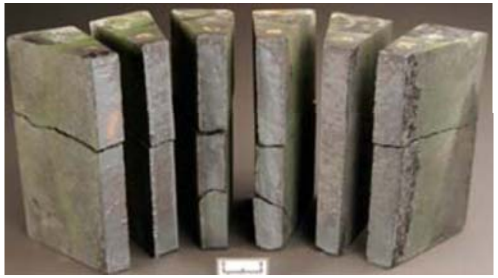
CO
H_2

By-products

H_2S
CO_2
Slag (Me-oxides)

Gas Clean-Up Before Product Use

Ref: Ronald W. Breault, National Energy Technology Laboratory, DOE



Conventional refractory
after
rotary slag testing

Type and abundance of "by products" strongly depends on the carbon source, eg. wood, straw, industrial waste etc., as well as the gasification temperature

Alkali-attacks (Na, K) are most abundant and severe

All silicate-based materials and binder phases are severely attacked in such applications.

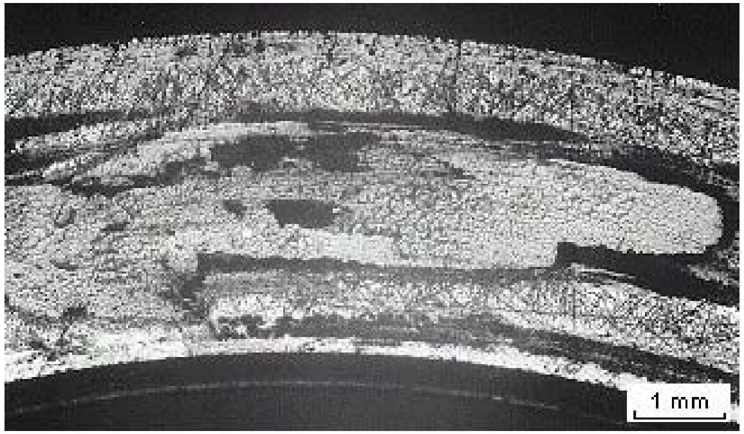
Alkali attacks runs through a combination of chemical reaction and pore penetration leading to spallation.

High Chrome-alumina bricks (neutral acidity) have shown acceptable service life for coal and wood gasification at high temperature (1250-1575^{0}C) good sulphur resistance.

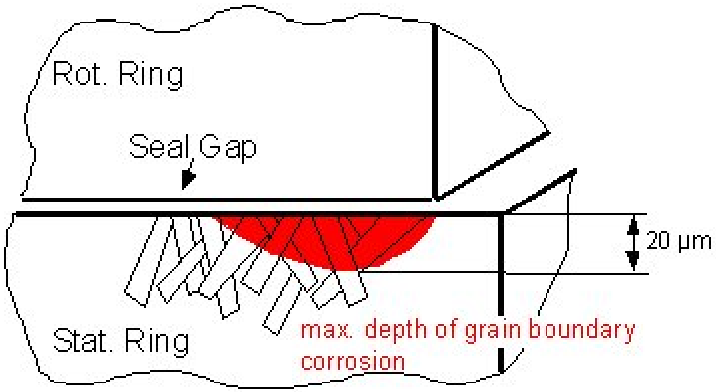
Fused and fused cast magnesia and magnesia-spinel bricks have shown good slag resistance in gasification at moderate and moderately high temperatures (600-1000^{0}C) of black liqueur.

Phosphate modified
high-chrome
oxide refractory
material

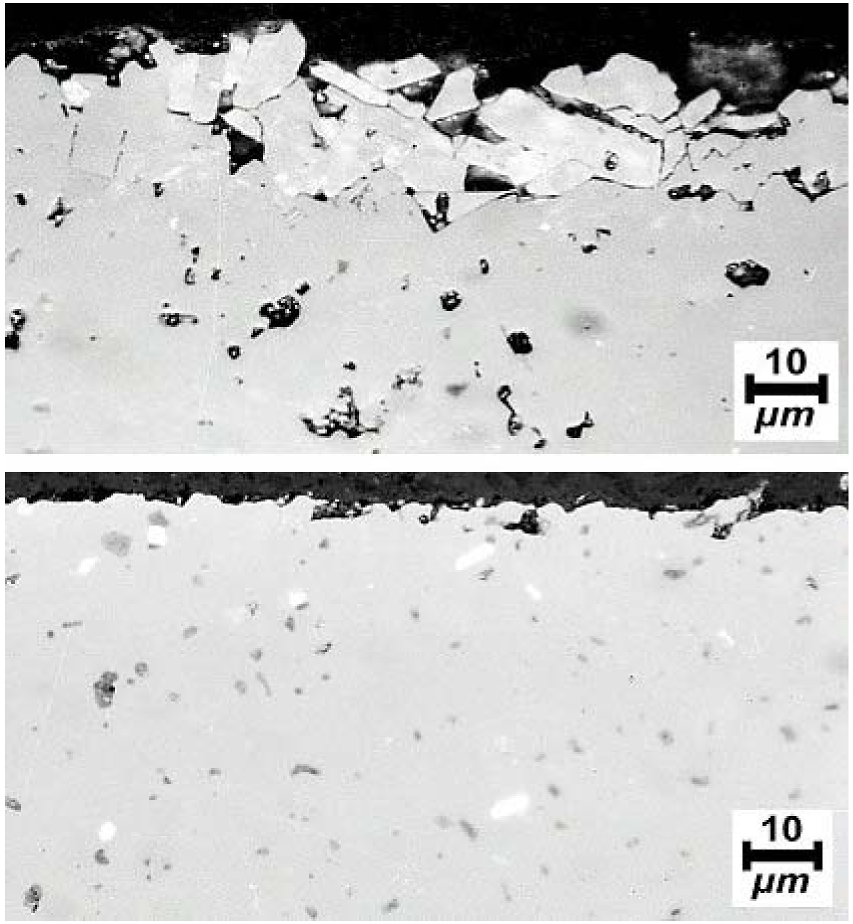
Corrosion of SiC bearings in aqueous environment



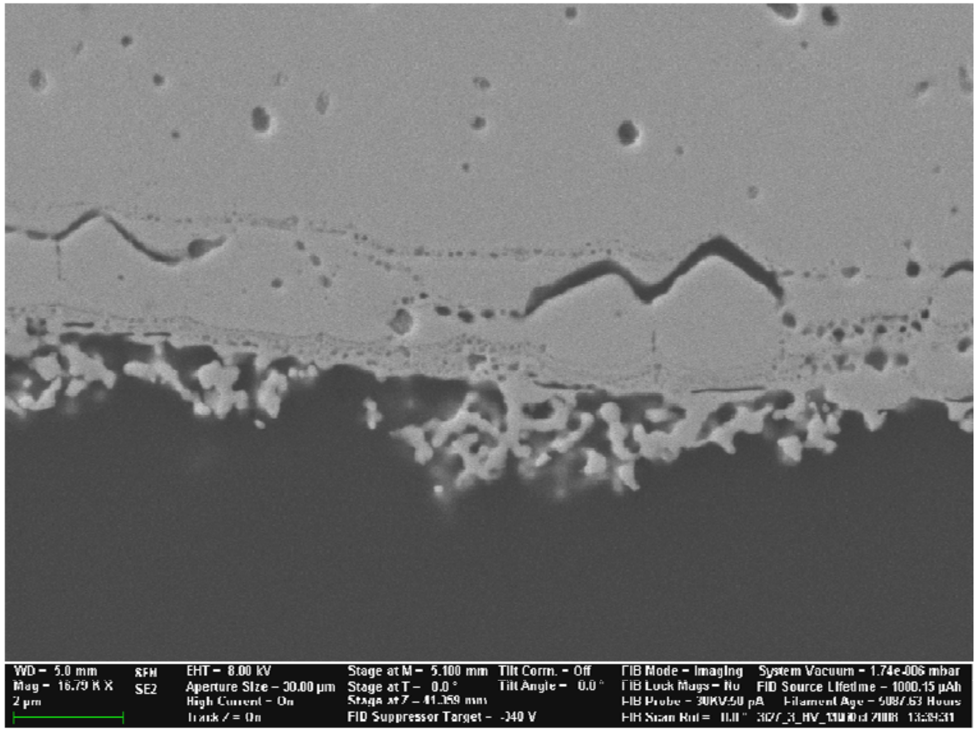
SiC plain bearing after 500 hr in demineralised water at 60°C.
Service life time: 1400-6500 hr



Run at 200°C for 20 hr –
UPPER: Conventional SiC-material
LOWER: SiC sintered at optimised conditions



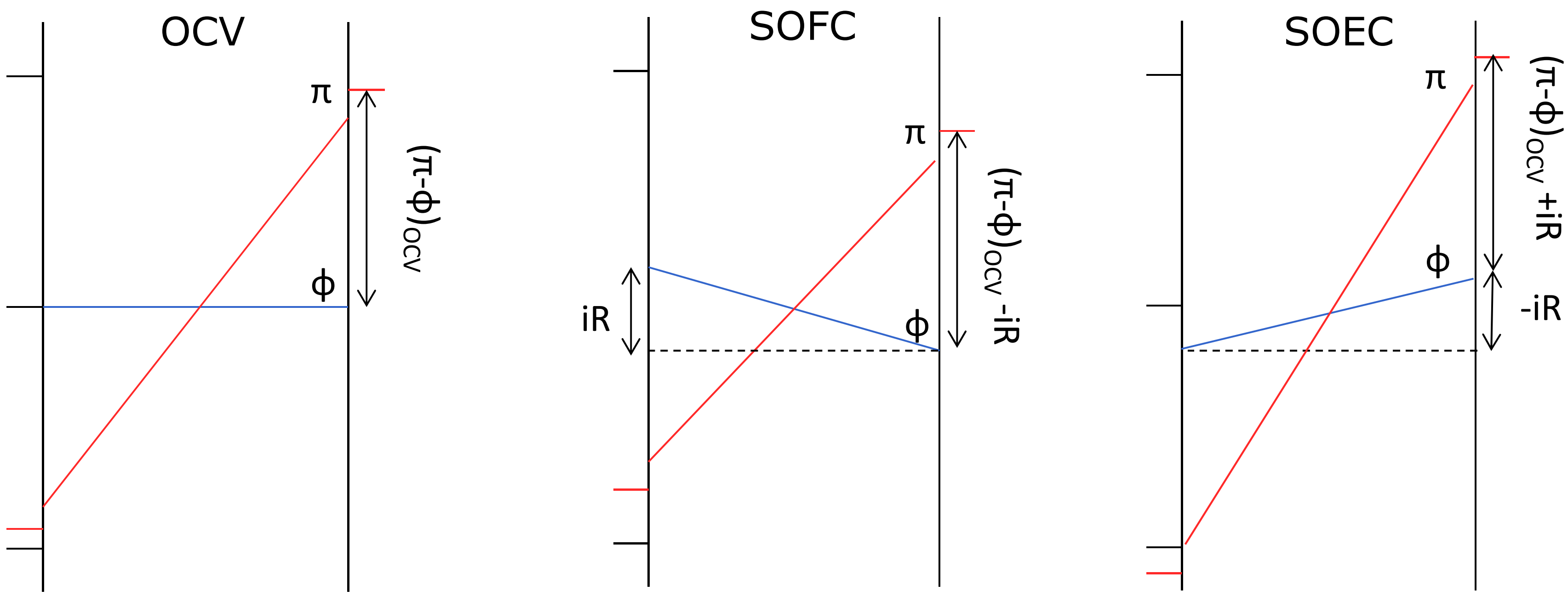
Degradation of stabilised zirconia electrolytes, when used in electrolysis cells under high current load (> ca. 1.3 A/cm^2@ 850°C)



- **Oxygen electrodes degenerate on SOE-cells during electrolysis at high current densities due to a high oxygen potential that builds up below the YSZ-surface, and at grain boundaries.**

- **Higher cation or hole diffusion may alleviate this**

Driving force for cation and hole migration

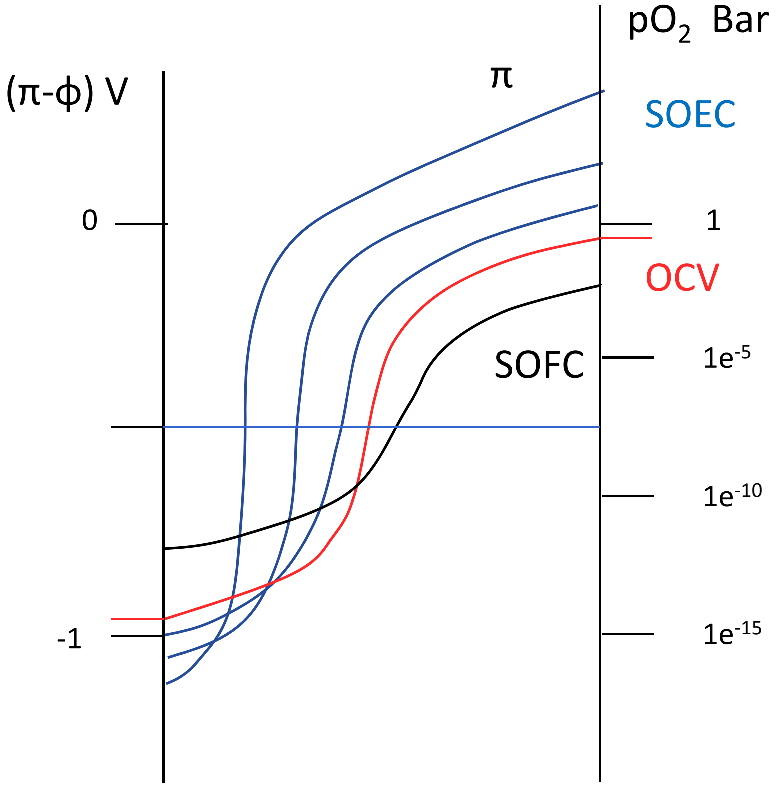


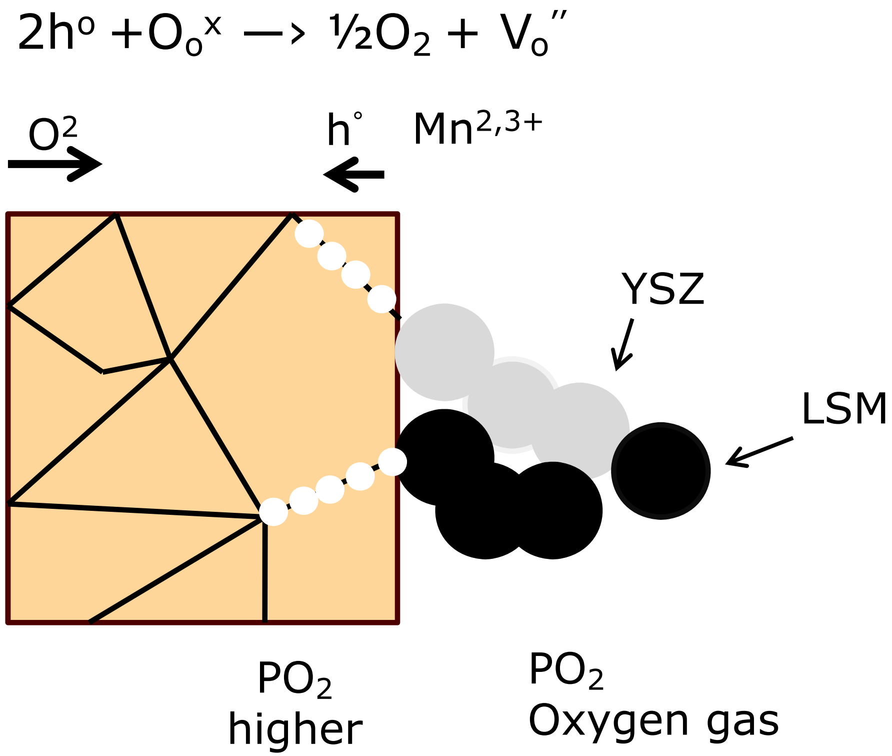
Π = electromotive potential = (μ_{e}-/F) - provides the driving force for electron (hole) migration

Φ = Galvani potential = (i/σ) – provides driving force for migration of oxide ions and the counter migration of cations.

T. Jacobsen & M. Mogensen (2008):

SOEC at high current density



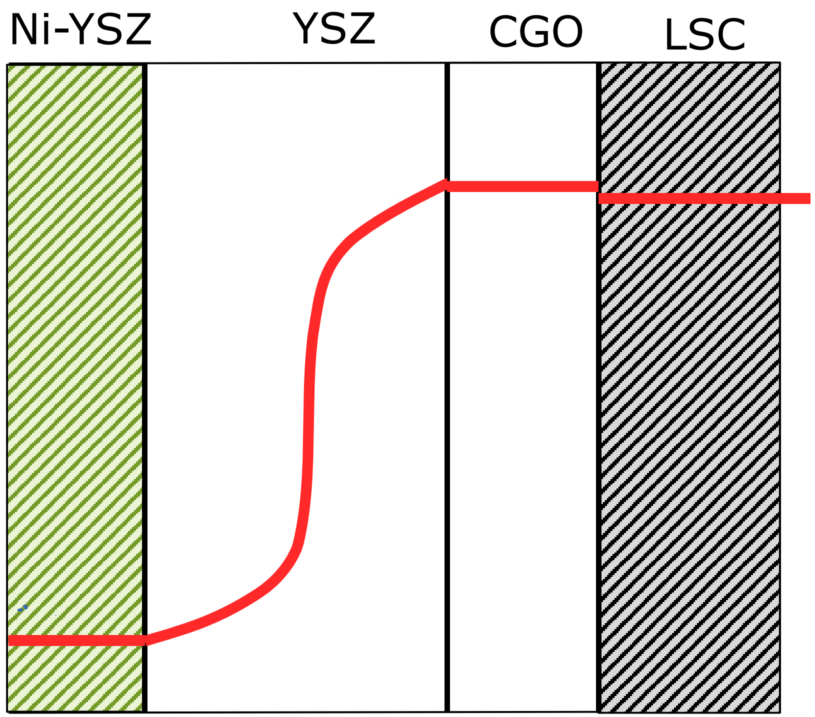


Grain boundaries:
- **high cation (Mn) diffusivity**
- **high hole conductivity**

Dr. C. Chatzichristodoulou

DTU Energy Conversion, Technical University of Denmark

A potential solution



Layer with higher
electron conductivity

CONCLUSIONS / Recommendations

- Seek information on the system, characterise if necessary
- Get information on the microstructure of the refractories
- Seek information with producers and similar applications
- Slag penetration, through open porosity and pore sizes, are important issues
- Warm water may be an aggressive medium
- Corrosion is often based on redox-, acid-base and solubility reactions
- Ceramics with mixed conductivity adds electrochemistry hereto

Thank you for your attention